$$Z_N = e^{3N\beta\epsilon}(6\beta\epsilon)^{-N}\frac{3\beta\epsilon}{\pi}$$
$$\times N^{1/2}\{\prod_{k\neq 0}(3-\cos k_x-\cos k_y-\cos k_z)\}\ . \quad \text{(B3)}$$

In the limit $N\to\infty$, the free energy, which is the logarithm of the partition function, is

$$\beta f = -3\beta\epsilon + \ln 6\beta\epsilon + \frac{1}{(2\pi)^3}$$
$$\times\int_{-\pi}^{\pi}\ln(3-\cos k_x-\cos k_y-\cos k_z)\,dk_x\,dk_y\,dk_z\ . \quad \text{(B4)}$$

The integral in (B4) is the $N\to\infty$ limit of the sum that is derived from the partition function by taking the logarithm of the product in (B3). Upon evaluating the integral, we can write the free energy per particle as

$$\beta\epsilon\,(f/3\epsilon) = -\beta\epsilon\ \tfrac{1}{3}\ln\beta\epsilon - 0.924\ . \quad \text{(B5)}$$

A simple check on this formula is to calculate the energy $\langle E\rangle = [\partial/\partial(\beta\epsilon)]\,\beta\epsilon(f/3\epsilon)$,

$$\langle E\rangle = -1 + 1/3\beta\epsilon\ , \quad \text{(B6)}$$

and compare it to an independent calculation of the energy. For N molecules with two degress of freedom, the low-temperature excitation spectrum is N independent harmonic oscillators, each having an energy $kT = 1/\beta$. Thus the total energy, including a normalization factor $|E_g| = 3N\epsilon$, is

$$\langle E\rangle = \frac{1}{3N\epsilon}\left(-3N\epsilon + \frac{2N}{2\beta}\right),$$

or

$$\langle E\rangle = -1 + 1/3\beta\epsilon\ . \quad \text{(B7)}$$

Thus our partition function satisfies this check and (B6) and (B7) both agree with our Monte Carlo results.

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Computer Simulation of Critical Properties and Metastable States in a Finite Square Ising System

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We report some results of a computer simulation of metastable states and critical properties in a finite Ising system consisting of square $n\times n$ lattices with and without periodic boundary conditions.

The description of metastable states on a fundamental level is both an interesting and unsolved problem in statistical mechanics.[1-3] Nature provides many examples of metastable states; they include supercooled vapors and liquids, supersaturated solutions, superheated liquid He^3,[4] ferromagnets in the part of the hysteresis loop where the magnetization and the applied magnetic field are in opposite direction, and diamond. Metastable states can occur in discontinuous phase transitions. Instead of making the appropriate phase transition, however, the system may go over continuously into a one-phase state, called a metastable state, which may have a very long lifetime. The distinguishing feature of a metastable state is that, eventually, either through external disturbances or spontaneous fluctuations which nucleate the missing phase, the system begins an irreversible process which leads to the new stable equilibrium state. The irreversibility of this transition corresponds to a decrease in free energy or an increase in entropy.[3]

In this paper we report some results of a computer simulation of metastable states and critical properties in a finite Ising model consisting of a square $n\times n$ lattice with and without periodic bound-

ary conditions. Our restriction to this model was dictated by a desire to compare some static critical properties with the exact results,[5] including the infinite system.[6] In these calculations we used the Monte Carlo method. This approach is somewhat analogous to observing physical quantities in a physical experiment. In the latter case nature provides the averaging, whereas in the mathematical experiment this is simulated by a model. However, in contrast to physical experiments, even the microscopic state itself may be an output at any moment during the calculations.

Since the model we discuss is essentially the same as that treated by several authors,[7,8] we merely write down some of the basic equations. We adopt the notations of Suzuki and Kubo,[8] except for trivial modifications. The master equation is

$$\frac{d}{dt}P(\sigma_1,\ldots,\sigma_N;t) = -\sum_j W_j(\sigma_1,\ldots,\sigma_j,\ldots,\sigma_N) \times P(\sigma_1,\ldots,\sigma_j,\ldots,\sigma_N;t) - W_j(\sigma_1,\ldots,-\sigma_j,\ldots,\sigma_N) \times P(\sigma_1,\ldots,-\sigma_j,\ldots,\sigma_N;t)\,. \quad (1)$$

The Hamiltonian is

$$\mathcal{H} = -\sum_{ij} J_{ij}\sigma_i\sigma_j - HNm\,, \quad (2)$$

where

$$J_{ij} = \begin{cases} J & \text{if } i \text{ and } j \text{ are nearest neighbor} \\ 0 & \text{otherwise}\,, \end{cases}$$
$$m = (\mu/N)\textstyle\sum_j \sigma_j\,. \quad (3)$$

The transition probability is given by

$$W_j(\sigma_1,\ldots,\sigma_N) = \tfrac{1}{2}\alpha\varphi = \tfrac{1}{2}\alpha\{1-\sigma_j \operatorname{th}[(H\mu+\textstyle\sum_k J_{jk}\sigma_k)/k_BT]\}. \quad (4)$$

Since $J/k_BT_c = \frac{1}{2}\ln(\sqrt{2}+1)$ in the infinite square lattice,[6] it is convenient to work with the scaled parameters T/T_c and H/T_c ($\mu = \mu_B$).

The quantity φ [Eq. (4)] may be evaluated with the Monte Carlo method, which has been described by several authors.[9,10] We note, however, [see Eqs. (1) and (4)] that the time scale is determined only up to a constant factor. In our calculations we express the time scale in units of the Monte Carlo steps per spin. The relevant quantities such as the mean magnetization $\langle m\rangle$ have been evaluated by a time average taken over a convenient time interval. For the isothermal susceptibility we used the relation

$$\chi_T = \left(\frac{\partial m}{\partial H}\right)_T = \frac{N}{k_BT}\langle(\Delta m)^2\rangle = \frac{\mu^2}{k_BTN}\langle(\textstyle\sum_i \sigma_i - \langle\sigma_i\rangle)^2\rangle\,. \quad (5)$$

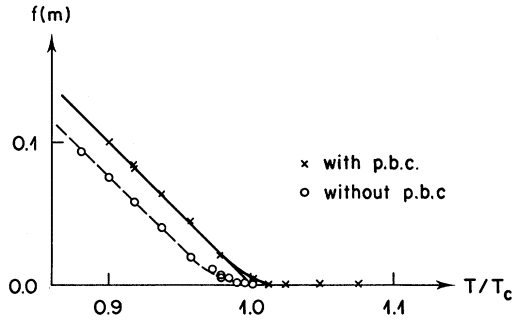

FIG. 1. Calculated spontaneous magnetization for a 110×110 square lattice

$$f(m) = 1 - \frac{\ln(\sqrt{2}+1)}{\ln(\{1+[1-(m/m_0)^8]^{1/2}\}^{1/2}+1) - \frac{1}{4}\ln[1-(m/m_0)^8]}\,.$$

It turned out that 10^4 Monte Carlo steps per spin for one set of extensive variables (H, T) led to accurate values of $\langle m\rangle$ and χ_T. However, this observation time appeared to be, even for small and antiparallel magnetic fields (antiparallel to $\langle m\rangle$), smaller than the umklapp relaxation time. Consequently, in this region, we also observed metastable states. The calculated spontaneous magnetizations of a 110×110 square lattice with and without periodic boundary conditions (PBC) are shown in Fig. 1. For comparison we also plotted (solid line) the rigorous behavior of the infinite square system.[6] It is seen that the finite system with PBC follows quite closely the behavior of the infinite system, except near to T_c, where the usual rounding associated with finite systems occurs. Without PBC there is a remarkable shift ($T < T_c$) towards smaller values of the ordinate. However for temperatures not too close to T_c, the slope is again equal to that of the infinite and finite systems with PBC, respectively. Similar behavior has been found (Fig. 2) in the temperature dependence of the isothermal and zero-field susceptibility. $1/\chi_T$ of the system with PBC simulates closely the behavior of the infinite system, namely, $(|\epsilon|)^{7/4} \sim 1/\chi_T$,[11] except near at T_c. This result also indicates that $\gamma \approx \gamma' \approx \frac{7}{4}$. The minimum occurs at $T > T_c$ as predicted by Ferdinand and Fisher.[5] Without PBC there is again a shift for $T < T_c$ towards smaller values of $1/\chi_T$, and for $T > T_c$ there is a shift towards larger ones. According to Ferdinand and Fisher[5] the minimum is expected at $T < T_c$. Due to the uncertainties in the calculated susceptibilities it appeared difficult to determine the position of the minimum unambiguously. $1/\chi_{T\,\min} > 0$ expresses the fact that in a finite system the mean-square fluctuations cannot grow without limits.

Figure 3 shows some results of the calculated equations of state for systems without PBC. First we discuss the stable regions. It is seen

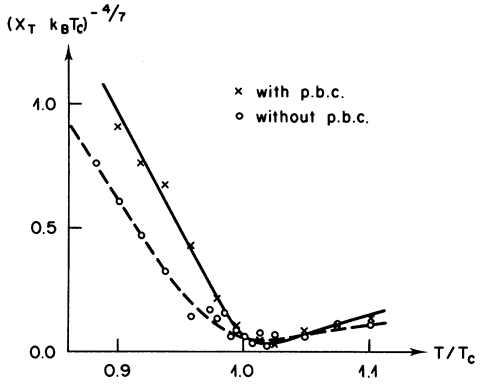

FIG. 2. Temperature dependence of the calculated zero-field susceptibility for a 110×110 square lattice.

that the magnetization for fixed T and H depends on the number of spins in such a way that $\langle m(H, T)\rangle$ decreases with decreasing N. We note that the susceptibilities derived from the equations of state agree quite well with those derived from the mean-square fluctuations (Fig. 2). The crucial point of these calculated equations of state is the appearance of metastable states. The lifetimes of these metastable states have been investigated over intervals of 10^4 Monte Carlo steps per spin. Within this interval no transition was observed for the plotted points. Of course the mean magnetization of the initial configuration was chosen antiparallel to the applied field. This situation corresponds to a physical experiment. For fields larger than the coercive field H_c the system underwent a first-order phase transition within 10^4 Monte Carlo steps. The temperature and field dependence of the lifetime of such states is shown in Fig. 4. We observe that the reciprocal lifetime decreases with decreasing field quite linearly. The lifetime extrapolates to infinity at our definition of the coercive field. Our results lead to the following relation between H_c and $\langle m(H_c)\rangle$:

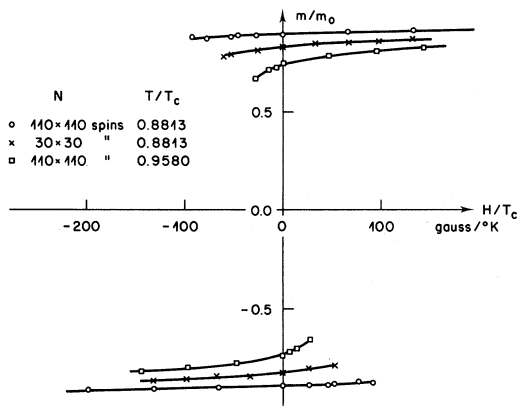

FIG. 3. Calculated equations of state without PBC.

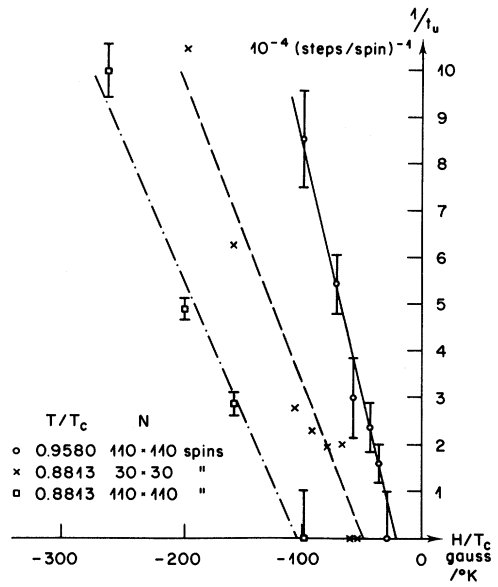

FIG. 4. Reciprocal lifetime of metastable states without PBC.

$$\langle m(H_c)\rangle^4 \sim H_c \ . \tag{6}$$

In analogy to the equations of state (Fig. 3) where H_c decreases with N and increasing T, we also ob-

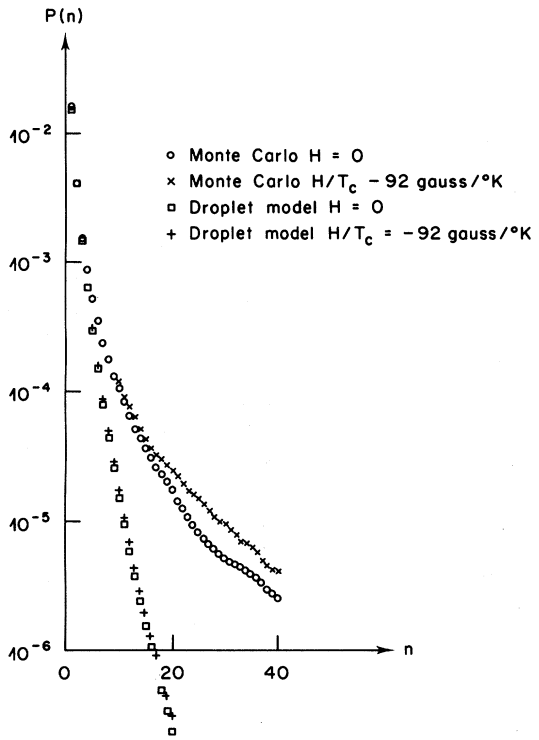

FIG. 5. Comparison of the calculated (without PBC) and predicted (spherical droplet model) cluster distribution.

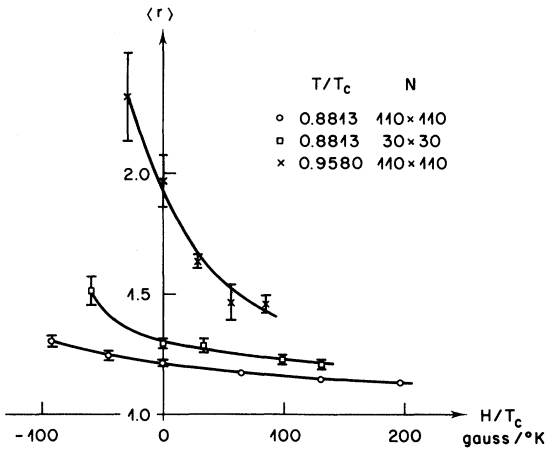

FIG. 6. Calculated mean cluster radius (without PBC).

serve a shift in the reciprocal lifetime.

To open a door towards better understanding of these metastable states we investigated the distribution of the spin clusters with spins parallel to the applied field. For this purpose we calculated the probability $P(n)$ for the occurrence of clusters consisting of n spins. These results are shown in Fig. 5. For comparison, we also included the predictions as obtained from Frenkel's[12] droplet model. According to this model one expects that

$$p(n) = p_0 e^{-\Delta\Phi/k_B T} , \tag{7}$$

where

$$\Delta\Phi = 2\mu Hn + \sqrt{32}\,[(n/\pi)^{1/2} + \tfrac{1}{6}]\,2J$$
$$= 2\mu Hn + \varphi(n) . \tag{8}$$

The first and second terms describe the "volume energy" and "surface energy", respectively. In this model possible anisotropy of the clusters is neglected. For small clusters there is remarkable agreement between the predictions of Eqs. (7) and (8) and our results (Fig. 5). However, with increasing n the disagreement becomes serious and indicates the importance of the cluster-border anisotropy which is neglected in Frenkel's droplet model. Perfect agreement may be obtained if the "surface energy" $\varphi(n)$ [Eq. (8)] is taken over from the computer simulation performed at $H = 0$. Clearly, this improvement is due to the inclusion of the cluster-border anisotropy. It then follows that the importance of the cluster-border anisotropy increases with increasing n. One expects that the first-order transition should occur if the cluster distribution $P(n)$ becomes sufficiently large for large clusters. To put this conjecture on a more quantitative basis we introduce the mean cluster radius $\langle r \rangle$ as a characteristic measure of the cluster distribution. In Fig. 6 we have plotted $\langle r \rangle$ as a function of H for different temperatures. Taking over the coercive fields from Figs. 3 and 4 we find the empirical relation

$$\langle r_c(T) \rangle^2 \sim 1/H_c(T) \sim 1/\langle m(H_c) \rangle^4 . \tag{9}$$

In the last step we used Eq. (6). Equation (9) states that the first-order transition occurs (within 10^4 Monte Carlo steps per spin) if the mean cluster radius exceeds a critical value $\langle r_c \rangle$. We note that $\langle r_c \rangle$ increases as T approaches T_c.

To summarize, we have reported on computer simulations of critical properties and metastable states in a square $n \times n$ Ising model. We find that the metastable states possess a long lifetime up to the coercive field and that the susceptibility is well behaved at the onset of long-lived metastability. It turned out that the homogeneous nucleation of the new phase depends on the occurrence of clusters with a critical size whose border anisotropy is of great importance. Our results also indicate that the use of PBC is of advantage (Figs. 1 and 2) if one is interested only in the values of the critical exponents of the corresponding infinite system.

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